

CHARACTERIZATION OF COAL SULFUR FUNCTIONAL FORMS  
BY PROGRAMMED-TEMPERATURE OXIDATION

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ABSTRACT

This paper describes the current status for characterization of coal by using a multiple sample controlled-atmosphere programmed-temperature oxidation (CAPTO<sub>m</sub>) instrument. Distinctive gas evolution patterns are observed among coals of different rank and between raw and treated coals. In addition to resolved SO<sub>2</sub> peaks, assignable to the oxidation of pyrite and the decomposition of sulfate, two others, assignable to organic structures in the coals, are observed. Coals from the Argonne Premium Coal Sample Program have been characterized by this technique.

INTRODUCTION

Interest continues to be strong in methods to reduce the levels of SO<sub>2</sub> and NO<sub>x</sub> in the atmosphere as a route to reduce acid deposition. This interest intensified development of advanced coal cleaning technologies which, in turn, generated a need for suitable analytical techniques to monitor progress of the work. A number of these analytical techniques, including CAPTO were reviewed in a previous report<sup>1</sup>. This work utilized a CAPTO instrument designed to characterize multiple coal samples in either an oxidative or pyrolysis mode. The instrument has been used in an oxidative mode to characterize the sulfur functional forms for the Argonne Premium Coal Samples.

EXPERIMENTAL

The CAPTO technique is used to characterize coals, treated coals, and other high molecular weight substances reduced to a particle top size of -60 mesh, or smaller. For oxidative characterization, the sample is thoroughly dispersed in a diluent (to reduce exotherms that occur during oxidation), inserted near the center of a quartz tube and positioned in a horizontal "primary" furnace. The sample is exposed simultaneously to a linear increase in temperature (normally 3°C/min) up to 1000°C and to a mass flow controlled oxygen stream of 100 mL/min. The gases flow through a catalytic "secondary" furnace held at 1050°C and through a heated transfer line for analysis using a Fourier Transform Infrared (FTIR) spectrometer equipped with multiple gas cells. The system shown in Figure 1 is designed to characterize four samples simultaneously. A single sample system has been previously described<sup>1</sup>.

Using the multiple sample CAPTO instrument in oxidative mode, characterization of the sulfur functionality was completed for the eight coals available from the Argonne Premium Coal Sample Program.

DISCUSSION

The distinctive gas evolution patterns observed among coals of different rank and between raw and treated coals have been related to the structural entity producing each peak<sup>1,2</sup>. The SO<sub>2</sub> evolution peaks obtained from oxidation of coal pyrite and decomposition of sulfate are resolved and appear at temperatures distinct from those observed from combustion of the organic

structures in coal<sup>1</sup>. Two major SO<sub>2</sub> evolution maxima resulting from organic structures are observed. Each of these peaks has CO<sub>2</sub> and H<sub>2</sub>O associated with it, implying that the organic matrix is oxidized in stages. Using model systems for comparison, these two major evolution maxima have been related to the probable structural types producing the evolutions. The temperatures observed for the evolution maxima are sensitive to the experimental conditions<sup>1</sup>.

Previous <sup>13</sup>C CP-MAS n.m.r. work<sup>2</sup> was completed on coal samples both before and after a CAPTO experiment that was terminated at 400°C. The n.m.r. spectra prior to the experiment indicated the presence of both aromatic and non-aromatic structures (f<sub>a</sub> = 0.69). After the sample was exposed to CAPTO conditions up to 400°C, the spectra revealed an essentially unchanged aromatic region; however, the non-aromatic region had been almost totally eliminated (f<sub>a</sub> = 0.87). Thus, the lower temperature CO<sub>2</sub> and SO<sub>2</sub> evolutions resulting from organic structures were attributed to carbon and sulfur lost primarily from oxidation of non-aromatic coal structures. The CO<sub>2</sub> and SO<sub>2</sub> evolutions from organic structures above 400°C were attributed primarily to carbon and sulfur lost during oxidation of the aromatic coal matrix. We still believe this to be a generally valid premise, and it is supported by the H/C ratio of 0.7 observed for the evolved gas at 400°C<sup>2</sup>. As also noted in the earlier work, stable aryl sulfides and sulfones oxidize above 400°C and should be included along with thiophenic structures in what we term "aromatic" sulfur.

The Argonne Premium Coal Sample Program coals were characterized using the multiple sample CAPTO instrument. One example, the absorbance/temperature CAPTO profiles for the Illinois No. 6 Argonne Premium Coal Sample is shown in Figure 2. The SO<sub>2</sub> evolution profile shows a peak at 274°C produced from oxidation of non-aromatic organic sulfur structures and a peak at 404 °C from the aromatic organic sulfur structures. The peaks at 439°C and 469°C are both derived from oxidation of pyrites and the small evolution at 580°C is produced from decomposition of iron sulfate. The CO<sub>2</sub> and H<sub>2</sub>O evolution profiles are also monitored and shown in Figure 2. Each profile shows a major peak related to oxidation of non-aromatic organic structures and aromatic organic structures. The ratio of non-aromatic/aromatic carbon or hydrogen is readily available from these profiles in addition to a continuous plot of the H/C ratio.

The relative areas of non-aromatic organic, aromatic organic, pyritic, and sulfate sulfur from the CAPTO evolution profiles were related to the ASTM total sulfur values of the Argonne coals for a comparison of sulfur forms. The preliminary results are shown in Table 1. As noted in Table 1 the Wyodak-Anderson and Beulah-Zap coals produced an additional SO<sub>2</sub> peak in the temperature range where SO<sub>2</sub> evolution from decomposition of several inorganic sulfates<sup>3</sup> is observed.

#### CONCLUSIONS

Quantitative studies are in progress to evaluate the CAPTO technique as a one-step determination of the organic, inorganic, and total sulfur present in coals and treated coals. The multiple sample CAPTO instrument has been used to characterize the sulfur forms of the Argonne Premium Coal Samples and the preliminary results are reported.

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Table 1

DETERMINATION OF SULFUR FORMS OF THE ARGONNE PREMIUM COALS  
RELATIVE TO ASTM TOTAL SULFUR (mf basis)

Argonne Premium Coal Sample	Wt% Total Sulfur	% Pyrite	% Non-Aromatic	% Aromatic	% Sulfate
Pocahontas #3, VA	0.66	0.09	0.13	0.44	nd.
Upper Freeport, PA	2.32	1.64	0.25	0.43	<0.01
Pittsburgh #8, PA	2.19	1.54	0.20	0.43	0.02
Lewis.-Stock., WV	0.71	0.26	0.08	0.37	nd.
Blind Canyon, UT	0.62	0.29	0.10	0.23	nd.
Illinois #6, IL	4.83	2.65	0.56	1.62	<0.01
Wyodak-Anders., WY*	0.63	0.19	0.11	0.15	0.02
Beulah-Zap, ND**	0.80	0.25	0.27	0.16	nd.

\* 0.16% Sulfur evolved at 832°C.

\*\* 0.12% Sulfur evolved at 756°C.

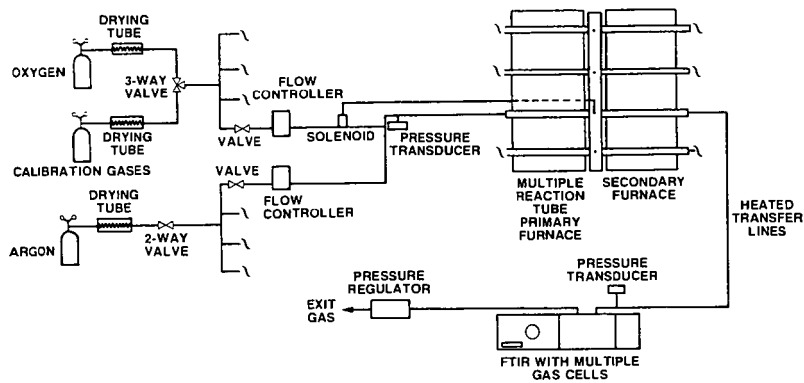


Figure 1. Flow system for the multiple sample controlled-atmosphere programmed-temperature oxidation (CAPTO) instrument.

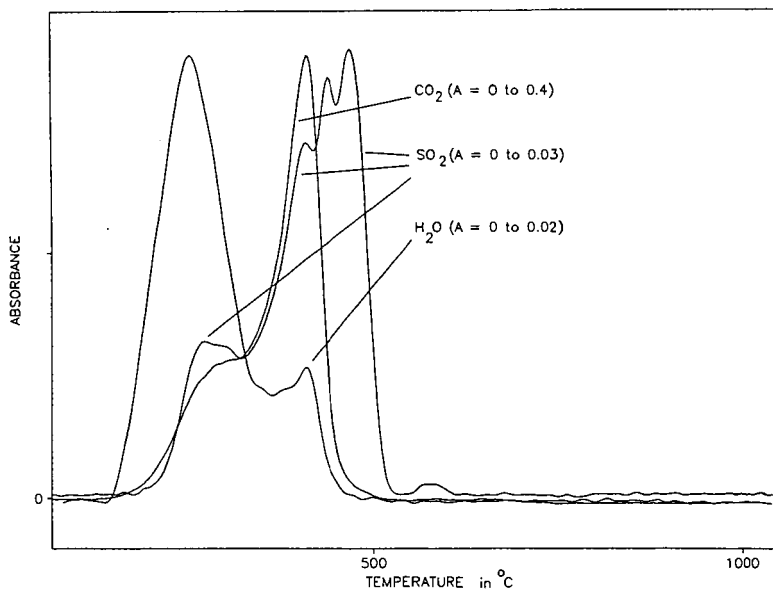


Figure 2. CAPTO evolution profiles from the Illinois No. 6 Argonne Premium Coal Sample.